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Determination of the chemical compounds and mineral contents in tomatoes (*Solanum lycopersicum* L.) grown under deficit irrigation conditions

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Abstract

The purpose of this study was to investigate the effect of deficit irrigation applications on the chemical compounds and mineral contents of tomatoes. In the study, a tomato (*Solanum lycopersicum* L) hybrid "Nehir F1" was grown in a greenhouse that had a natural light, heating and ventilation system and was covered with polycarbonate material. The tomatoes were irrigated every three days by applying 60% (T1), 80% (T2), 100% (T3) and 120% (T4) of the evaporation value after reading and determining it from the reduced evaporation pan. The tomatoes were harvested at the red-ripe maturity stage and analyses were performed. As a result of the study a total of 60 compounds were determined in the tomato samples by using Gas chromatography/Mass Spectrometer system. The most abundant compounds in terms of both amount and variety in the tomatoes were identified as ketones, sugars and fatty acid esters. Furthermore, the mineral content of the tomatoes changed according to the irrigation application. K, Mg, P, Ca and Fe were accumulated in the all tomatoes samples.

Keywords: Tomato; *Solanum lycopersicum*; Deficit irrigation; Chemical compound profile; Mineral content; GC-MS

1. Introduction

Tomatoes (*Solanum lycopersicum*), which are a nutritious and delicious vegetable, are cultivated and consumed in many countries around the world [1,2]. The annual global production of tomatoes, which are cultivated in thousands of varieties, has exceeded 160 million tons [3]. It is the most cultivated vegetable in Turkey. According to the data of the Turkish Statistical Institute (TSI), the production tomatoes under protective cover in 2017 was 3.83 million tons. This value corresponds to approximately half of the total production that was cultivated under cover around the world. In addition to having early and late varieties, tomatoes can be consumed in all seasons as they are produced in greenhouses. Due to their rich antioxidant and vitamin content and their different uses in the kitchen, the consumption of tomatoes is high [2]. Tomatoes are mostly consumed fresh or as various value-added products such as juice, paste, sauce, puree and ketchup [4].

Tomatoes contain various nutrients and antioxidants [1,2] including vitamins E, C [5] and A, riboflavin, thiamin, pantothenic acid, niacin, pyridoxine, minerals (calcium, magnesium, phosphorus, potassium, sodium, zinc, manganese, and others), phenolic acids, flavonoids, lycopene, β-carotene and glycoalkaloids (tomatine) [6], flavonoids and phytosterols [7]. Furthermore, tomato products are rich flavonoids, folate, dietary fibers, protein [5]. The consumption

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of tomatoes can prevent many diseases due to the various antioxidants, including carotenoids (lycopene and β-carotene) vitamin K, tocopherol, Fe, phenolic acids and flavonoids they contain [8,9,10].

Recently, the increase in the world population has increased agricultural activities. This increment has caused an increase in water consumption and consequently water resources have begun to diminish. In addition, climate change has also limited water resources due to the rise in average temperatures. The scarcity of water during crop sowing season not only causes a decrease in crop productivity but also economic loss for farmers. The amount of water given to a produce depends on commercial and functional quality, environmental and agronomic conditions, as well as leaf water potential, turgor, water content, productivity, fruit size, soluble solids, carotenoid and phenolic content and flavor properties [11].

A large number of studies have determined that tomato plants grown in fields or under protective cover were very rich in terms of nutrients [12,13,14,15,16,17,18]. Studies have been conducted on the limited use of water or deficit irrigation and water use efficiency for the production of tomatoes [19,20,21,11]. Most of these studies focused on the effect of the lack of water on yield and irrigation efficiency and found that deficit irrigation conditions caused a reduction yield but an increase in water use efficiency. In the literature, there are limited studies carried out to identify the combined effect of deficit irrigation conditions and the nutrient content of tomatoes [22,23,24]. To best of our knowledge, there is a literature gap concerning the effect of deficit irrigation on the chemical compound and mineral content of tomatoes by using GC-MS. Therefore, the objective of this study was to fill this gap by investigating the effects of deficit irrigation application on the chemical compounds and mineral content of tomatoes grown in greenhouse conditions.

2. Material and methods

2.1. Material

In the present study tomatoes (*Lycopersicon esculentum* L. cv. "Nehir F1") were chosen as the studied material. Crop production was performed in the Atatürk University Agricultural Structures and Irrigation Department Education and Research Greenhouse, which has natural light heating and ventilation system and is covered with polycarbonate material.

The tomato seeds were planted in crate type pots that were 50cmx80cmx42cm in size and each pot contained a total of five plants. The growing medium was formed with 60% soil, 20% peat, 10% sand and 10% perlite. One kg of burnt farmyard manure was mixed into each pot. The investigation was carried out in a completely randomized block design with three replicates. The tomatoes were irrigated every three days by applying 60% (T1), 80% (T2), 100% (T3) and 120% (T4) of the evaporation value after reading the reduced evaporation pan. The analyzes were conducted with the tomatoes in the red-ripe maturity stage gathered from the 3rd harvest.

2.2. Sample preparation for the Gas chromatography/Mass Spectrometer system (GC-MS)

Five grams of fully ground fresh tomatoes and 50 mL of methanol were mixed together with a magnetic stirrer in an Erlenmeyer flask for chemical compound extraction at room temperature for 12 hours. This mixture was passed through filter paper and then a syringe filter (22 µm). Then 1 µl solution was employed to the GC-MS system.

2.3. The GC-MS system and the method conditions

The GC-MS analyses of the tomato extract was carried out with a Agilent 7820A gas chromatography system equipped with a 5977 series mass selective detector, 7673 series autosampler and chemstation (Agilent Technologies, Palo Alto, CA). An HP-5 MS capillary column (30 m × 0.25 mm internal diameter, x 0.25 µm film thickness, USA) was used for separation. The temperatures of the inlet, transfer line and detector were 250, 250 and 300 °C, respectively.

The method development for the assay of the phytocomponents was based on their chemical properties. In this study, a capillary column coated with 5% phenyl and 95% dimethylpolysiloxane was preferred for the separation of these analytes as they elute as symmetrical peaks at a wide range of concentrations. Different temperature programs were investigated for the GC oven and the best temperature program was selected for good separation. The temperature programs of the GC oven were as follows: the initial temperature was 50 °C, raised for 1 min, then raised to 100 °C at a rate of 20 ºC/min for 1 min, then raised to 180 °C at a rate of 10 ºC/min for 1 min, increased to 220 °C at a rate of 5 ºC/min for 5 min, and finally to 300 °C at a rate of 5 ºC/min for 5.5 min. The injection volume was 1 µl in the splitless mode and high purity helium was used as the carrier gas at a constant flow rate of 1 ml/min.

2.4. Identification of Compounds

The identified chemical compounds were determined with the National Institute of Standards and Technology (NIST) Library Version (8), Software, Turbomass 5.2 and standard reference materials. The compounds were identified by comparing the linear Kovats retention index and mass spectra with those obtained from the MS library. The interpretation of the mass spectrum GC-MS was conducted using the database of the NIST, which was comprised of more than 62,000 patterns. The relative percentage area of each compound was calculated by comparing its average peak area to the total areas. The name and molecular weight of the chemical compounds were detected.

2.5. Inductively coupled plasma mass spectrometry analysis (ICP-MS)

The analysis of the mineral elements Potassium (K), Magnesium (Mg), Phosphorus (P), Calcium (Ca), Aluminum (Al), Iron (Fe), Manganese (Mn), Zinc (Zn) and Sodium (Na) in the tomato samples was performed by using an Inductively Coupled Plasma/Mass Spectrometer (Agilent 7800 ICP-MS) [25]. The tomatoes were made into pulp by using a blender. Approximately 0.5 g of the pulp was weighed directly in PTFE tubes to which 8 ml of 65% HNO3 and 2 ml of 31% H2O2 were added. This mix was kept at room temperature for 15-20 minutes. Then, the tubes were placed into a digestion oven at 200 °C for 30 minutes until the solution became clear. After the solution was cooled to room temperature, ultrapure water was added to make the final volume of 50 mL. The contents of the tubes were filtered through a 0.45 µm membrane filter. 100 µl of this filtrate was taken and made up to 10 ml with a mixture of 2% HNO3 and 0.5% HCl. This mixture was then analyzed. The blank solutions were prepared similarly.

3. Results and discussion

3.1. Effects of deficit irrigation conditions on the chemical compounds of tomatoes

The chemical compound profiles of the tomatoes grown with the deficit irrigation applications were obtained by using GC-MS. The peaks within the chromatogram were incorporated and then compared with the database of the spectral range of known compounds presented in the NIST library. As a result of the GC-MS analyzes 22, 12, 13 and 13 different chemical compounds were identified in the 60%, 80%, 100% and 120% irrigated tomatoes, respectively. The retention time (RT) and relative area percentages of the identified chemical compounds are summarized in Table 1. A total of 31 compounds were detected in the tomato samples including, epoxide, esters, alcohol, alkene, amides, a steroid derivative, ketones, thioester, acid, oxime derivative, a piperidine derivative, sugars, a sugar derivative, fatty acid esters, vitamins , organic nitrate, inden derivative, an amino acid derivative, purine nucleoside and an unknown compound. The most abundant compounds in terms of both amount and variety in the tomatoes were sugars, ketones and fatty acid esters (Tables 1). The results demonstrated that the chemical compound profiles of the tomatoes changed with the water application. As shown in Table 1, the maximum compounds (22 compounds) were found in the tomatoes irrigated at 60%. Twenty-one of these chemical compounds were positively identified, while one was unidentified. Twelve compounds were detected in the tomatoes irrigated at 80%, while 13 compounds were determined in the tomatoes irrigated at 100% and 120%. Butane, 1,2:3,4-diepoxy-, (+/-.)- and 4-Hydroxy-2,5-dimethyl-3-furanone, and pyranone, and α-Tocopherol were present in all of the tomatoes irrigated at different levels. Pyranone was found as 23.41%, 29.74%, 22.67% and 9.25% in the tomatoes that were irrigated at 60%, 80%, 100% and 120%, respectively. Melezitose, β-lactose, DL arabinose and d-glycero-d-ido-heptose were determined as the aroma-active sugar compounds in the different tomato extracts. Sugars and acids contribute to the aroma of tomatoes [26]. These compounds are desired to be high and balanced. The sugar and organic acid contents in tomatoes depend on the development and ripeness of the tomatoes. The organic acid content is developmentally controlled and increases during ripening [27].

Studies have found that esters are the most significant aroma compounds in fruits [28]. In the present study 1,2,3-propantriol, 1-acetate were present in the tomatoes irrigated at 60%, 80%, and 100%. The tomatoes that were irrigated at 100% contained a high proportion of octadecanoic acid 2-hydroxy-1-(hydroxy-methyl) ethyl ester (37.81%) (Table 1). Octadecanoic acid, 2,3- dihydroxypropylester was found in the tomatoes irrigated at 120% at a percentage of 53.44% (Table 1). Ripe tomatoes produce many volatile compounds, and most of these are related to aroma and derived from essential nutrients including amino acids, essential fatty acids and carotenoids [9].

4-Hydroxy-2,5-dimethyl-3-furanone was observed in all of the tomatoes irrigated at different levels while 2-Furanmethanol was found in the tomatoes irrigated at 60% as ketones (Tables 1). Furaneol, also known as furanone, has an intense caramel-like aroma. It is an important aroma compound as it has a low odor threshold value. Furaneol is naturally biosynthesized in plants, fruits and microorganisms by multistep enzymatic reactions. In addition, it is formed in different concentrations during Maillard reactions and some thermally processed foods including tomatoes, grapes, pineapples, soy sauce, roasted coffee and roasted almonds [29,30,31,32].

Table 1 Chemical compounds detected in the methanol extract of the tomatoes irrigated at 60% (T1), 80% (T2), 100% (T3) and 120% (T4)

Peak number	Class of chemical compound	Chemical compound	Retention time (min)	Relative peak area (%)			
				T1	T2	T3	T4
1	Epoxide	Butane, 1,2:3,4-diepoxy-, (+/-.)-	3.27	3.50	3.62	1,34	1,49
2	Alcohol	1-Butanol, 2-nitro	3.34	0.92	-	-	-
3	Thioester	Propanoic acid, 3-(acetylthio) -2-methyl	3.44	2.92	2.50	0.26	-
4	Ketone	2-Furanmethanol	3.81	0.90	-	-	-
5	Acid	2,3-Bis (acetyloxy) succinic acid	3.87	0.22	-	-	-
6	Oxime derivative	Oxime-methoxy-phenyl	4.00	3.80	-	0.22	2.94
7	Acid	Propionic acid-(acetylthio)-2-methyl-(s)-	4.29	1.83	-	-	-
8	Epoxide	6-Oxa-bcyclo [3.1.0] hexan-3-one	4.38	1.42	-	-	-
9	Ketone	4-Hydroxy-2,5-dimethyl-3-furanone	5.83	5.58	2.93	2.35	2.41
10	Sugar	d-Glycero-d-ido-heptose	5.68	4.83	2.38	8.17	-
11	Piperidine derivative	4,4'biscyclohexanone,2,2',6,6'-tetra methyl-	6.12	0.74	-	-	-
12	Alkene	2-Nitro-1-buten-3-ol	6.96	1.81	2.67	1.58	-
13	Ketone	Pyranone	7.08	23.41	29.74	22.67	9.25
14	Organic nitrate	Isosorbide dinitrate	7.88	2.19	12.29	-	11.58
15	Sugar derivative	Melezitose	8.32	2.34	-	-	-
16	Ester	1,2,3-Propantriol,1-acetate	8.59	28.37	37.86	16.04	-
17	Sugar	β-Lactose	9.35	8.29	-	-	-
18	Amid	1-Nitro-2-acetamido-1,2-dideoxy-d-glucitol	11.87	0.66	-	-	-
19	Steroid derivative	17β-Estradiol, 3-deoxy	18.61	0.43	-	-	-
20	Fatty acid ester	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester	29.69	3.22	-	3.97	6.26
21		unknown	34.81	0.66	-	-	-
22	Vitamin	α-Tocopherol	36.26	1.95	1.21	0.99	0,67
23	Purine nucleoside	Guanosine	4.05	-	1.50	-	-
24	Sugar	DL-Arabinose	4.29	-	1.79	-	3.29
25	Fatty acid ester	Hexadecanoic acid, 2,3- dihydroxy propyl ester	29.69	-	1.51	-	-
26	Ester	Butan edioic acid, 2,3-bis (acetyloxy)-	3.41	-	-	1.22	1.64
27	Inden derivative	1-n-Hexadecylindan	32.19	-	-	3.39	5.71
28	Fatty acidy ester	Octadecanoic acid 2-hydroxy-1-(hydroxy-methyl) ethyl ester	32.34	-	-	37.81	-
29	Amide	1-Nitro-2-acetamido-1,2-dideoxy-d-mannitol	5.72	-	-	-	0.63
30	Amino acid derivative	Alfa-acetyl-L-serine	6.95	-	-	-	0.69
31	Fatty acidy ester	Octadecanoic acid, 2,3-dihydroxypropylester	32.35	-	-	-	53.44

The tomatoes that were irrigated at 60% contained the highest percentage α-Tocopherol (Table 1). Vitamin E is a common term used for a group of tocopherol and tocotrienol that are soluble in fat. Plant oils, various kinds of margarine, nuts, eggs, whole grain cereal and various fruits and vegetables (e.g. broccoli) contain vitamin E. This vitamin shows antioxidant activity and prevents oxidative stress, cardiovascular diseases, cancer, cataracts and Alzheimer's disease. Furthermore, vitamin E improves nerve conduction, maintains the integration of hemoglobin membranes and together with vitamin A, is important for healthy eyesight [33].

In the present study, it was found that the irrigation application factor affected the chemical compounds profiles of the tomatoes. Similarly, a previous study determined that the genotype of tomatoes and the production system significantly influenced the composition of volatiles such as aroma compounds [10]. The volatile compounds of tomatoes have been found to be affected by many factors such as genotype, growing conditions, maturity, growing season, harvest time, and post-harvest treatments [34,9,10]. Wang et al (2016) detected volatile compounds in the pericarp and locular gel of red FL 47 and Tasti-Lee tomatoes by headspace, solid-phase micro-extraction, and gas chromatography-mass spectrometry system (HS-SPME/GC-MS) and mostly found aldehydes, hydrocarbons, alcohols, ketones, oxygen-containing heterocyclic compounds, esters, nitrogen compounds and b sulfur- and nitrogen-containing heterocyclic compounds [35]. In a study conducted on cherry tomatoes a total of 49 volatile compounds were identified and quantified [36]. Another study also identified 49 volatiles in tomatoes [2]. Lee et al (2019) determined that tomatoes contained 40 volatiles that included alcohols, aldehydes, esters, fatty acids, furans, hydrocarbons, ketones, and sulfur compounds [10]. In a previous study, 18 volatile compounds were quantified and identified from headspace samples of tomatoes [34].

3.2. Effects of deficit irrigation conditions on the mineral content of the tomatoes

The tomatoes samples contained the following minerals: K, Mg, P, Ca, Al, Fe, Mn, Zn and Na (Table 2). The quantities of these minerals changed in accordance with the irrigation application applied to the tomatoes. The results showed that the K concentrations in the tomatoes were relatively higher than the concentrations of the other minerals. In Table 2 it can be seen that the concentrations of K, Ca and Fe in the samples that were irrigated at 60% were higher than the concentrations found in the other tomato samples. In addition, it can be concluded that the tomatoes irrigated at 120% had higher K and Mg concentrations compared to the other tomato samples. It was determined that Al, Mn and Zn had only accumulated in the tomatoes irrigated at 120%. K, Mg, P, Ca are essential macro-elements and on average an adult requires more than 100 mg/day, while Fe and Zn are the second essential trace element with adults requiring less than 100 mg/day [37].

Table 2 The mineral content of tomatoes according to the irrigation applications (ppm)

Mineral	T1 (60%)	T2 (80%)	T3 (100%)	T4 (120%)
K	38272.05	30038.36	23912.11	20712.72
Mg	1745.65	1003.71	1627.68	2709.90
P	3760.49	3325.31	3878.24	5381.04
Ca	821.06	549.51	495.33	403.72
Al	Nd	Nd	Nd	415.76
Fe	388.03	58.37	36.11	129.26
Mn	Nd	Nd	Nd	1.19
Na	Nd	Nd	Nd	83.94
Zn	Nd	Nd	Nd	41.86

Nd: not determined

4. Conclusion

The results of this study demonstrated that the chemical compounds of the tomatoes were significantly influenced after different irrigation applications were applied. GC-MS was used to analyze the chemical compounds in the tomatoes and it was determined that a total of 60 chemical compounds were present in the tomatoes. Pyranone was identified as the dominant ketone in the tomatoes and was followed by d-glycero-d-ido-heptose. Pyranone was detected in all of the tomato samples and its content ranged from 9.25 to 29.74% in the tomato samples. In addition, the results showed that the mineral contents of the tomatoes depended on the applied irrigation system. The K concentrations in the tomatoes were relatively higher compared to the other minerals. Al, Mn, and Zn were found to have only accumulated in the tomatoes irrigated at 120%.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no conflicts of interest.

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